

The Corrosion of Tungsten During Irradiation in an 800 MeV Proton Beam

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INTRODUCTION

Corrosion of solid neutron spallation targets such as tungsten (W), and target cladding or structural materials such as superalloys and stainless steels, is a significant concern in accelerator-driven technologies. One such technology is Accelerator Production of Tritium (APT). In APT a tungsten target is bombarded by a high energy (800 MeV or greater) proton beam operating at a current density of 1 mA or greater. When these protons collide with W nuclei, neutrons are generated. To moderate the energy of these spallation neutrons (to increase the efficiency of the He3 capture reaction) the W target is immersed in a cooling water loop which also provides temperature control. In this paper we describe our current efforts to characterize the corrosion of W in accelerator cooling water loops. Data presented includes experiments in laboratory simulated environments and real time measurements in an 800 MeV proton beam using floating, electrochemical impedance spectroscopy (EIS).

EXPERIMENTAL

Potentiodynamic polarization curves and EIS measurements were performed on 99.96% bcc W samples. Prior to testing all samples were polished to 0.3 micron alumina finish followed by a chemi-mechanical 0.06 MasterMet (pH 10.5) to remove any work hardening.

Experiments were conducted in 0.1M NaCl (pH approx. 5) and buffer solutions consisting of : 0.1M tartaric acid pH 2, 0.5M boric acid / 0.05M sodium borate pH 7.2, 0.025 sodium borate / NaOH pH 10.6. Unless noted otherwise, all experiments were conducted in quiescent solutions at room temperature. Potentiodynamic polarization curves were generated at a scan rate of 0.1 mV/sec. EIS measurements were generated at 0.0V vs SCE (Saturated Calomel Electrode).

In-beam experiments were conducted at the Los Alamos Neutron Scattering Center, Weapons Neutron Research facility. This facility provided easy access to a proton beam for our conventional three electrode electrochemical cell. At the WNR facility the proton beam measures approximately 1 cm in diameter and has an energy of 800 MeV, a macropulse characteristic repetition rate of 20Hz and, a macropulse length of 625 microseconds. Beam currents were controlled by varying the spacing between each micropulse in the macropulse. Nominally, the currents varied between 50 and 500 nA.

In-beam corrosion experiments on W at WNR were conducted in 0.10M NaCl. The cell was designed to allow a flow (via a peristaltic pump) through the cell at a rate of 1.0 L/min. This was done to

minimize heating of the sample due to deposition of energy from the proton beam. As a result, the solution remained at room temperature throughout the in-beam experiments.

RESULTS AND DISCUSSION

Anodic potentiodynamic polarization curves for W as a function of pH were characterized by active dissolution in the potential region between OCP and 0.0V vs SCE. No passivity was found independent of solution pH. For solution pH less than or equal to 5, anodically limited dissolution (limiting current $2 \times 10^{-5} \text{A/cm}^2$) was observed at more positive potentials. This finding is contradictory to the Pourbaix diagram which indicates at solution pH less than 6 and at more positive potentials oxide formation (WO_4 , W_2O_5 , WO_6) passivates the surface. For solution pH 10.6, anodically limited dissolution currents were on the order of 10^{-3}A/cm^2 .

The OCP for W in the WNR flow cell as a function of time prior to turning the beam on is shown in Figure 1. When the proton beam was turned on (2 nA beam current) to align the cell with the beam a small positive shift in the OCP from its steady state value of -0.305V SCE to a value of -0.295V SCE was observed. After alignment, the OCP began to decrease to its original value. As shown in Figure 1, soon after alignment the proton beam was turned on at 50 nA. Correspondingly, a large increase in the OCP was observed. While the OCP for W shifted to more positive potentials with increasing beam current, the absolute change decreased and appeared to plateau around -0.220V SCE.

While positive shifts in the OCP with increasing proton beam current is an indication of increasing corrosion rate at the OCP, this shift may owe to changes in the concentration of cathodic reactants. Specifically, water radiolysis products such as hydrogen peroxide are cathodic reactants. Therefore, to determine whether or not proton beam interactions with W/Wox effect the anodic reaction kinetics, changes in the metal dissolution rate at an applied anodic potential of 0.0V SCE with beam current were measured. As shown in Figure 2 this potential is clearly in the anodic portion of the polarization curve for W in 0.1M NaCl. Although the anodic dissolution rates for W in Cl⁻ solutions was somewhat less than in buffer solutions no passivity was observed in Cl⁻ solutions.

EIS magnitude plots for W measured at 0.0V SCE and several representative proton beam currents are presented in Figure 3. The impedance is plotted on a linear scale for clarity. Both the Bode magnitude and phase plots revealed two time constants for the W system. As shown in this figure the low frequency at 0.0V SCE decreased with increasing proton beam current. After the irradiation period, EIS data was collected for an additional 12 hours. During this period the charge transfer resistance gradually returned to its pre-irradiation value. Upon removing the W sample from the electrochemical cell it was gray/black and appeared to be roughened. Because the surface radioactive contamination of the sample was extremely high after these experiments

(approximately 4 rads/hr) no other examination (SEM, EDX) was done.

The in-beam EIS results demonstrate conclusively that the mechanism by which corrosion rates are increased during proton irradiation include an increase in the anodic dissolution rate. Increased temperature, due to energy deposition, is one possible mechanism for the observed increased dissolution rates. To evaluate temperature effects energy deposition and thermalhydraulic calculations are currently in progress. From these calculations the temperature at the electrode surface can be determined within several degrees Celcius. However, the observation that the test solution remained at room temperature and that 12 hours were required for the charge transfer resistance to return to its pre-irradiation value is a strong indication that thermal consideration are not an issue.

This paper will address other possible mechanisms including:

- damage from spallation products
- changes in the structure of the oxide:
 - oxide resistivity
 - point defects
 - diffusion rates

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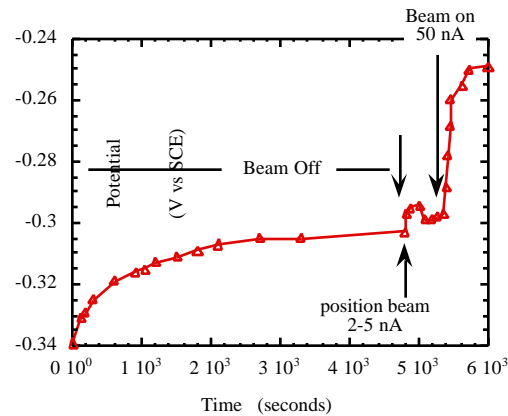


Figure 1 OCP vs time for W in 0.1M NaCl with flow of 1 L/min. Figure shows the OCP prior to irradiation and during irradiation by an 800 MeV proton beam at 50 nA.

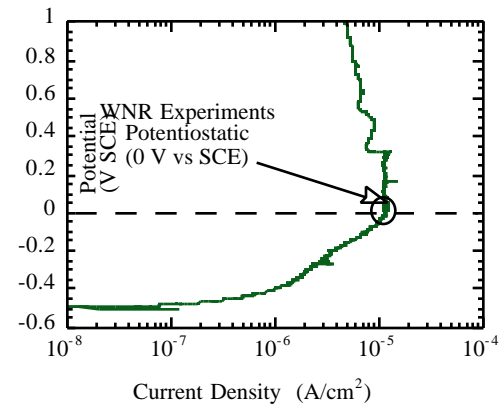


Figure 2 Potentiodynamic polarization curve for W in 0.1M NaCl. No flow was employed during this experiment.

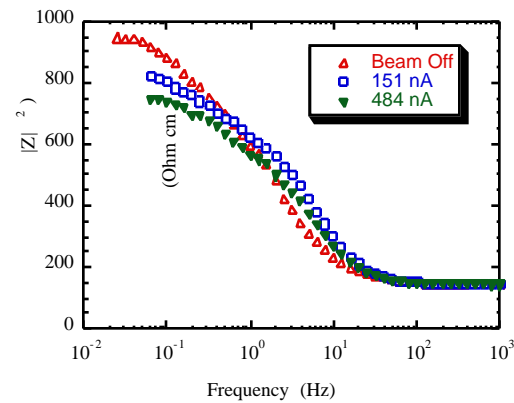


Figure 3 EIS plots depicting the magnitude of the impedance (linear scale) as a function of proton beam current during irradiation. Data were taken in 0.1M NaCl with a flow rate of 1 L/min. “Beam Off” data were taken prior to turning the proton beam on.